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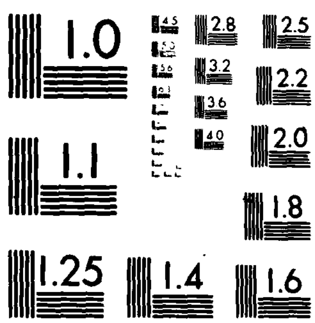

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AN EVALUATION OF THE TOXIC HAZARD ASSOCIATED WITH THE USE OF A FLUORESCENT PARTICLE ATMOSPHERE TRACER IN AN URBAN AREA.

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TABLE OF CONTENTS

AN EVALUATION OF THE TOXIC HAZARD ASSOCIATED WITH THE USE OF A FLUORESCENT PARTICLE ATMOSPHERE TRACER IN AN URBAN AREA

H.D. Madill and J.J. Norman

ABSTRACT

The toxic hazard from the use of a fluorescent particle atmosphere tracer containing cadmium sulfide within and near the city of Winnipeg in 1953 was evaluated. From the airborne concentrations of this tracer measured in thirty-two separate tests, it was concluded that no toxic hazard to cadmium was produced. In all of the tests, the maximum concentrations measured were less than the current limits of safe occupational exposure to this compound. The maximum amount of cadmium sulfide which could have been inhaled was only 14 to 55 percent of the average daily dietary intake of cadmium normally assimilated by the people of an industrialized country.

AN EVALUATION OF THE TOXIC HAZARD ASSOCIATED WITH THE USE OF A FLUORESCENT PARTICLE ATMOSPHERE TRACER IN AN URBAN AREA

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Introduction

An atmospheric tracer may be any distinctive substance released into the air which is then used to study atmospheric flow and the transport of airborne material. The dissemination of tracer material, at or near the ground surface, is used to study the micro-meteorological conditions existing over widely differing surface environments. These may vary from open unobstructed terrain to densely populated urban areas. The information obtained from such studies may then be utilized to predict the spread of airborne pollutants such as gases, aerosol partculates that arise from exhaust emissions, or airborne micro-organisms. An example of the application of models developed from such meteorological research is found in the prediction of the spread of chlorine gas released from the rupture of a railway tank car in the city of Mississauga in 1979. As a result of being able to rapidly predict the consequences of this event, 250,000 people were safely evacuated away from the toxic hazard.

Fluorescent Particle (FP) Tracers

In the period immediately following World War II, work was undertaken in the United States to develop atmospheric tracers to study atmospheric flow patterns. In the following two decades, numerous materials were employed for this purpose as reported by Leighton et al (6). Some of the materials which have been utilized are: oil fog, *Lycopodium* spores, sulfur dioxide gas, radioactive Xenon 138, antimony oxide, uranine dye and inorganic fluorescent particulates.

The criteria which must be met by a suitable atmospheric tracer are as follows: it must possess a specific property making it distinctive in normal atmosphere for ease of detection; the measurement of the material must be simple, rapid and convenient for purposes of quantitating its presence in small amounts; it should be stable, uniform, readily available and economical; it must be dispersible at quantitative controlled rates; it should remain stable in the atmosphere and possess properties of atmospheric diffusion similar to that of an inert gas; it should retain its specific properties throughout its travel through the atmosphere and during assessment; and of principal importance, it must be safe to handle and be non-toxic to man, animal or plant life.

Research undertaken at Stanford University, under contract to the United States Army between 1946 to 1955, centered upon the utilization of fluorescent inorganic particles as atmospheric tracers. The specific tracer which was developed and used extensively was a mixture of zinc and cadmium sulfides (2-6).

Zinc-Cadmium Sulfide (FP) Atmospheric Tracer

The fluorescent particle (FP) tracer comprising a mixture of zinc sulfide and cadmium sulfide has been widely used in atmospheric studies (1-7). The substance used, designated as FP2266, was initially made by the New Jersey Zinc Company and later by the United States Radium Corporation in New Jersey. This compound is widely used as a paint pigment and, when combined with small amounts of other elements, it is employed for its luminous properties in paints for signs.

FP is a finely-powdered product consisting of particles with sizes ranging between 1 to 5 μm in diameter. The mixture is approximately 20% cadmium sulfide and 80% zinc sulfide; thus it contains 0.16 g cadmium per g of FP (8, 16). The material selected for atmospheric studies has a mass median diameter ranging between 2.0 μm and 3.0 μm in diameter with an estimated density of the particle mixture reported to be 4.0 (4).

Toxicity of Zinc-Cadmium Atmospheric Tracer (FP)

One of the principal requirements of an FP product is that it be non-toxic to human, animal and plant life. In the FP product (FP2266), the cadmium sulfide component is of primary toxicological concern. The current safe occupational exposure limits for cadmium oxide and zinc oxide are reported as 0.05 mg/m^3 and 5.0 mg/m^3 respectively (9). The limit for zinc oxide is the same as that for an inert nuisance dust, and because of the similar inert properties of zinc sulfide, the toxicity of this portion of the FP product will be disregarded.

Occupational exposure limits are reported as Threshold Limit Values - Time Weighted Averages (TLV-TWA). The TLV and TWA are synonymous and represent concentrations of chemical substances over an 8-hour work day or 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effects (9). These values are subjected to periodic review and continually amended on the basis of the current state of knowledge of the toxicity of each compound.

A review was published by the U.S. National Institute of Occupational Safety and Health in 1976 (10) to establish the recommended standard for occupational exposure to cadmium and cadmium

compounds. These toxicity limits apply to cadmium dust and salts (including cadmium oxide). The comparative toxicological literature indicates that a greater hazard exists for these compounds than for cadmium sulfide (13). For this reason, it is safe to apply the published TLV-TWA occupational exposure limits for cadmium dusts and salts to cadmium sulfide.

In the case of cadmium salts and dust, a short term exposure limit (STEL) of 0.2 mg/m^3 is permitted (9). The short term exposure limit is defined as the maximum concentration to which workers can be exposed for a period up to 15 minutes continuously without causing ill effects, provided that not more than four such excursions are encountered per day and that at least a 60-minute period has elapsed between each excursion. This same short term exposure limit thus applies to cadmium sulfide.

The principal source of cadmium is the ore greenockite which is primarily cadmium sulfide. The element occurs in economically recoverable amounts only with the sulfide ore of other elements, particularly zinc; thus the natural form of commercial cadmium is of similar composition to that of the FP tracer.

Prior to the utilization of the zinc cadmium sulfide FP product as an atmospheric tracer, the known information on its toxicity was reviewed (4). No adverse effects were reported following the inhalation exposure of dogs to a concentration of 4.0 mg/m^3 cadmium sulfide aerosol, over periods which averaged 895 hours (11). These results are in agreement with the findings of a previous occupational study carried out in 1947, in which humans were reported to have been temporarily exposed to cadmium sulfide concentrations ranging between 18 to 31 mg/m^3, without suffering acute ill effects (12).

These early studies provided the necessary toxicological information to demonstrate that the zinc cadmium sulfide FP atmospheric tracer was safe to use in inhabited areas.

The FP product of common usage by Leighton, FP2266, had a mass median diameter of 3.0 μm. With a partial density of 4.0 (4), one gram of FP thus contains 1.7×10^{10} particles. Based upon the current TLV-TWA of 0.05 mg/m^3, the equivalent exposure concentration for FP particles would thus be 0.85×10^6 particles/m^3 with a corresponding STEL of 3.4×10^6 particles/m^3. A similar association for the determination of FP exposure limits had previously reported a TLV-TWA limit of 10^7 particles/m^3 (8). Given that the FP product does not contain more than 20% cadmium sulfide, the corresponding TLV-TWA and STEL then become 4.25×10^6 particles/m^3 and 17.0×10^6 particles/m^3, respectively.

Winnipeg Atmospheric Tracer Studies

During the period of 9 July to 3 August 1953, a series of 36 atmospheric tracer trials were conducted within the city of Winnipeg and one of the immediate surrounding rural areas. The results of these trials are documented in a report prepared by Leighton of Stanford University and the Ralph M. Parsons Company in 1953 (15).

Of the 36 trials carried out, results were presented for only 32 in this report. In the remaining four trials, wind shifts occurred and the tracer material never reached the samplers.

The series of trials consisted of single point releases, two point releases with the aerosol generators spaced 110 to 335 yds apart and line releases over 1.6 to 5.0 miles. Seven of the trials were performed in open country 18 miles outside of Winnipeg in the region of Stony Mountain, with the remaining twenty-five trials carried out in the center of the city.

During the trials, the tracer FP2266 was disseminated by a blower at rates ranging from 2.0-5.3 g/min at the single or double point sources and at a rate of 18 to 63 g/min from a mobile blower on the line source disseminations. In each trial, sampling points were distributed down wind, with the distances from the source ranging from 50 ft to over 4000 yds. The particles were collected on filters by means of flow-calibrated pumps which sampled the atmosphere at a rate of 10 l/min. Samples were taken at 5 min consecutive intervals at the sampling points which received the highest concentrations. In all of the trials, over 95% of the cloud had passed each of the closest sampling points with 10 to 15 min.

A summary of the trial results extracted from the original report (14) is presented in Table I. The maximum FP dosages are expressed as particle min/l of air for each of 32 tests. Only the highest dosages are reported. These were obtained from those sampling positions in the closest downwind position to the source. These dosages represent the integration of all the consecutive 5 min sample particle concentrations over the duration of the passage of the cloud and represent a dosage to which an individual would be exposed if he were at the same location as the sampler.

The safe occupational exposure limits for aerosol compounds such as that FP product used in the Winnipeg study are expressed as mg/m^3 concentrations (9). As previously pointed out, the equivalent TLV-TWA or STEL occupational exposure limits for FP2266 may be expressed as particles/m^3 . In terms of the cadmium sulfide component of this product, these limits are: TLV-TWA 4.25×10^6 particles/m^3 and STEL 17.0×10^6 particles/m^3.

A review of Table I indicates that in no instances were the concentrations found to exceed the short term exposure limit, STEL, and in only two cases, during trial 2013b conducted in the Stony Mountain region outside of the city and one test (2006c) in the city, did the values exceed the TLV-TWA.

Although comparisons of the concentrations achieved during this trial have been made with the accepted occupational exposure limits for industrial workers, it is important to emphasize that the TLV-TWA values are based upon a continuous exposure over a worker's career. In the case of the Winnipeg tracer study, the longest exposure period was from 10 to 15 minutes; thus a further safety factor of at least three orders of magnitude is provided by comparing these short term exposures to a chronic exposure period of one year, based upon a 40 hour work week for 48 working weeks.

From the highest concentration levels reported in Table I (test 2013b), where average concentrations of 4.95×10^6 and 6.08×10^6 particles/m^3 were reported, it is possible to estimate the potential human dose. A human walking at a moderate rate may breathe 20/1 of air/min. Over the 10 min period of cloud passage, this equals 0.2 m^3 or 0.99×10^6 to 1.22×10^6 particles of FP. Each particle contains 11.3×10^{-6} μg of cadmium sulfide. If the assumption is made that all of the particles inhaled were retained in the lungs, the total dose of cadmium taken in would then be 11.2 and 13.8 μg as cadmium sulfide. These amounts are only 14 to 55 percent of normal daily dietary cadmium intake of individuals in most industrialized countries (16).

A large amount of literature concerning the toxicity of cadmium and its salts has been accumulated over the last 45 years. This literature was thoroughly reviewed to provide the best judgement in establishing a safe occupational exposure limit (10,16). When the current safe occupational exposure limits are applied to the results of the 1953 trials, it is concluded that no toxic hazard was presented to humans in the downwind path of this FP aerosol.

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TABLE I

Atmospheric Tracer Study, Winnipeg, 1953

FP dosages and average concentrations at sampling points yielding highest readings

Test	Date	Source	FP Released g	Release Period min	Wind Speed mph	Time of Day	Sampling point dosages, Particle min/L	Average Cloud Concentration based upon a 10 min passage, Particles/L	STEL 17 X 10^6 particles/m^3 Average concentration of FP particles/m^3 X 10^6
2001a	9 July	single pt ground	24.0	5.0	0.9	21:10	7180 3010 1200 3790 10,000 2140 2130	718 301 120 379 1,000 214 213	0.72 0.30 0.12 0.38 1.00 0.21 0.21
2001b	9 July	single pt roof	13.3	5.0	5.0	22:29	1060 2100 2245	106 210 224	0.12 0.21 0.22
2001c	9 July	single pt	14.9	5.0	2.0	23:35	3950 1470	395 147	0.39 0.15
2002a	11 July	single pt ground	13.4	5.0	3.7	00:23	495 335 221 146	49 33 22 15	0.05 0.03 0.02 0.01
2002b	11 July	single pt roof top	16.7	5.0	6.0	01:47	952	95	0.10
2002c	11 July	2 pts 110 yd apart	18.5 17.0	5.0	3.5	02:35	1110 1440 9360 13,200	111 144 936 1,320	0.11 0.14 0.94 1.32

TABLE I cont.

Atmospheric Tracer Study, Winnipeg, 1953

FP dosages and average concentrations at sampling points yielding highest readings									STEL 17 x 10^6 particles/m^3
Test	Date	Source	FP Released g	Release Period min	Wind Speed mph	Time of Day	Sampling point dosages, Particle min/L	Average Cloud Concentration based upon a 10 min passage, Particles/L	Average concentration of FP particles/m^3 X 10^6
2005c	12 July	Line Source 1.7 miles	194.3	10.8	4.1	23:05	2,090 1,560 2,150 860	209 156 215 86	0.21 0.16 0.21 0.09
2006a	25 July 25 July	Line Source 1.6 miles	308.5	6.67	6.9	13:05	29,700 12,500 11,400 1,270 38,200 7,700	2,970 1,250 1,140 127 3,820 777	2.97 1.25 1.14 0.13 3.82 0.78
2006b	25 July	2 pts 200 yd apart ground	26.0 14.3	5.0	4.8	14:46	744	74	0.07
2006c	25 July	Line Source 1.6 miles ground	364.1	7.78	5.8	15:50	14,800 3,110 6,620 47,200 3,070 8,470 2,790	1,480 3,110 662 4,720 307 847 279	1.48 0.32 0.66 4.72 0.31 0.85 0.28
2008a	14 July	1 pt ground	22.1	4.5	2.3	22:45	2,770 9,870	277 987	0.28 0.99
2008b	14 July	1 pt roof top	21.1	5.0	7.6	23.50	1,160 1,630	116 163	0.12 0.12
2008c	15 July	2 pts 220 yd	16.1 12.9	5.0	3.1	01:05	6,950 1,430	695 143	0.69 0.14
2009a	23 July	Line 3.3 miles	610.4	14.45	3.1	20.35	2,890 2,890 2,120	289 289 212	0.28 0.29 0.20

TABLE I cont.

Atmospheric Tracer Study, Winnipeg, 1953

FP dosages and average concentrations at sampling points yielding highest readings									STEL 17 X 10^6 particles/m^3
Test	Date	Source	FP Released g	Release Period min	Wind Speed mph	Time of Day	Sampling point dosages, Particle min/L	Average Cloud Concentration based upon a 10 min passage, Particles/L	Average concentration of FP particles/m^3 X 10^6
2003a	12 July	single pt ground	18.0	5.0	4.3	21:20	17,800 3,840 502	1,780 384 50	1.78 0.38 0.05
2003b	12 July	single pt roof top	10.1	5.0	8.2	13:20	8,320	832	0.83
2003c	12 July	2 pts 115 yd apart	14.0 13.5	5.0	4.0	14:35	3,300	330	0.33
2004a	12 July	2 pts 335 yd apart	22.8 18.1	5.0	1.2	22:45	15,500 2,243 1,220 1,160	1,550 224 122 116	1.55 0.22 0.12 0.12
2005a	12 July	Line Source 1.7 miles	365	9.13	3.3	21:05	13,700 11,200 7,440 1,270 4,640 2,900 1,480	1,370 1,120 744 127 464 290 148	1.37 1.12 0.74 0.13 0.46 0.29 0.15
2005b	12 July	2 pts 230 yd apart ground	25.2 14.9	5.0	4.7	22:10	32,600	3,260 88	3.26 0.09

TABLE I cont.

Atmospheric Tracer Study, Winnipeg, 1953

FP dosages and average concentrations at sampling points yielding highest readings | STEL 17 X 10^6 particles/m^3

Test	Date	Source	FP Released g	Release Period min	Wind Speed mph	Time of Day	Sampling point dosages, Particle min/L	Average Cloud Concentration based upon a 10 min passage, Particles/L	Average concentration of FP particles/m^3 X 10^6
2009b	23 July	Line Source 3.3 miles	491.0	15.4	3.5	23.07	1,690	169	0.17
							1,490	149	0.15
							2,309	231	0.23
2010a	30 July	Lines Source 1.6 miles	321.7	7.77	1.9	21:35	19,300	1,930	1.93
							1,245	124	0.12
							34,300	3,430	3.43
							28,500	2,850	2.85
							4,200	420	0.42
							10,250	1,025	1.02
							1,700	170	0.17
							64	6.4	0.006
							25,100	2,510	2.51
							10,800	1,080	1.08
2010b	30 July	2 pts 280 yd apart ground	17.1 2.4	5.0 4.5	2.4	01:25	1,070	107	0.11
2011a	3 Aug	2 pts ground	16.6 23.2	5.0	9.0	20:57	1,955	195	0.19
							4,160	416	0.42
							1,379	138	0.14
							1,128	113	0.11
2011b	3 Aug	Line Source 3.1 miles	786	12.47	5.0	21:45	6,670	667	0.67
							5,900	590	0.59
							4,780	478	0.48
							10,200	1,020	1.02
							8,870	887	0.89
							7,940	794	0.79
							6,400	640	0.64
2012a	3 Aug	2 pts 180 yd apart ground	26.5 24.7	5.0	4.1	22:47	8,600	860	0.86
							7,300	730	0.73
							3,288	329	0.33
							1,133	113	0.11
							1,020	102	0.10

TABLE I cont.

Atmospheric Tracer Study, Winnipeg, 1953

FP dosages and average concentrations at sampling points yielding highest readings									STEL 17 X 10^6 particles/m^3
Test	Date	Source	FP Released g	Release Period min	Wind Speed mph	Time of Day	Sampling point dosages, Particle min/L	Average Cloud Concentration based upon a 10 min passage, Particles/L	Average concentration of FP particles/m^3 X 10^6
2012b	3 Aug	1 pt	23.3	5.0	4.5	23:48	1,520	152	0.15
2013a	2 Aug	2 pts 185 yd apart	14.6 10.4	5.0	6.9	14:35	20,000 20,000	2,000 2,000	2.00 2.00
2013b	2 Aug	Line Source 3.2 miles	530	12.98	5.0	16:20	12,000 49,500 60,800 13,700 1,060 740 860 5,930 1,020 2,010 1,267	1,200 4,950 6,080 1,370 106 74 86 593 102 201 127	1.20 4.95 6.08 1.37 0.11 0.07 0.09 0.59 0.10 0.20 0.13
2013c	2 Aug	2 pts 185 yd apart ground	12.5 9.0	5.0	5.0	17:20	20,000 14,900	2,000 1,490	2.00 1.49
2014a	1 Aug	Line Source 5.0 miles	630	21.92	6.1	12:35	1,000	100	0.10
2014b	1 Aug	Line Source 5.0 miles	600	22.5	4.3	14:50	1,000	100	0.10